The influence of relative humidity on the ion (proton) conductivity of the intramolecular polycomplexes

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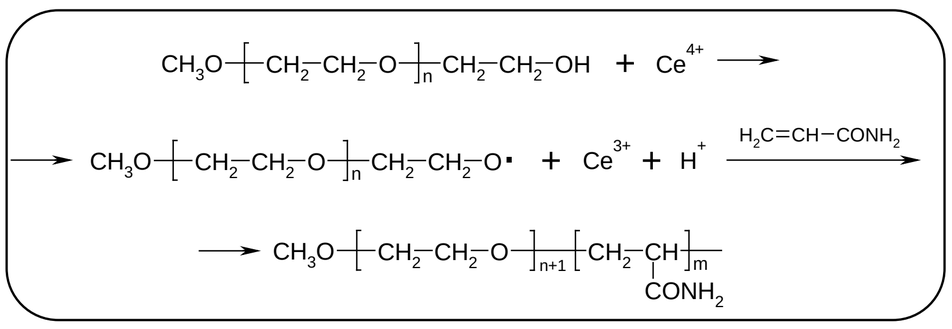
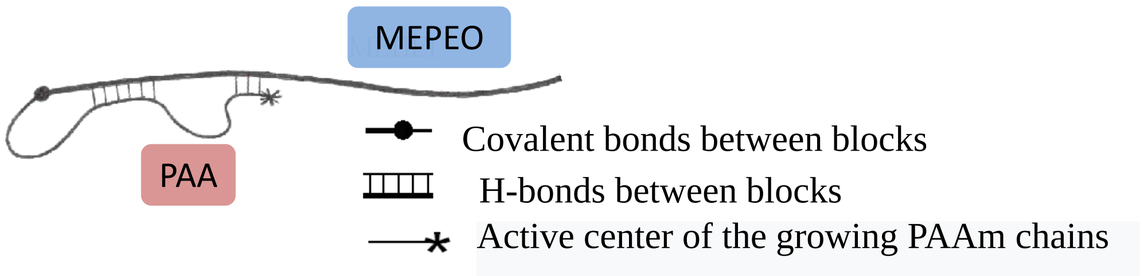
The problem of the energy crisis is contributing to the increasingly active search for the alternative ways to obtain energy, including fuel cells. A solid polymer electrolytes (SPEs) with high ionic conductivity at room temperature has been an importance subject due to their interest in the all solid-state electrochemical devices development.

In the present study, block copolymers comprising chemically complementary poly(ethylene oxide)/polyacrylamide have been evaluated as proton conducting materials. With this aim in mind, two series of block copolymers PAAm-*b*-PEO (DBC) and PAAm-*b*-PEO-*b*-PAAm (TBC) with the variable PEO-block length and also their partially hydrolyzed derivatives (DBC_{hydr} and TBC_{hydr} respectively) were prepared by using a solution casting technique, and their ion (proton) conductivity was studied at the ambient temperature and at different relative humidity (RHIn the present study, block copolymers comprising chemically complementary poly(ethylene oxide)/polyacrylamide have been evaluated as proton conducting materials. With this aim in mind, two series of block copolymers PAAm-*b*-PEO (DBC) and PAAm-*b*-PEO-*b*-PAAm (TBC) with the variable PEO-block length and also their partially hydrolyzed derivatives (DBChydr and TBChydr respectively) were prepared by using a solution casting technique, and their ion (proton) conductivity was studied at the ambient temperature and at different relative humidity (RH).

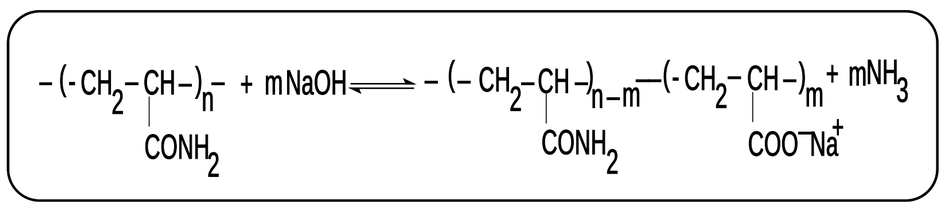
Synthetic methods for producing conductive polymers which form IntraPCs



Synthesis of DBCs by the radical block copolymerisation of acrylamide and methyl ether of poly(ethylene glycol).
To obtaine TBCs the poly(ethylene glycol) were used.



IntraPC formation in DBC



Introduction of -COOH-groups into DBCs /TBCs chains lead to obtain DBC_{hydr} and TBC_{hydr}

Table 1 - Molecular parameters of block copolymers found by ^1H NMR spectroscopy

Copolymer	MnPEO, kDa	MnPAAm, kDa	MnDBC/TBC , kDa
DBC1	0.75	11	11.75
DBC2	2	30	32
DBC3	5	241	246
DBC_{hydr}	5	196	248
TBC1	6	968	974
TBC2	14	1040	2100
TBC3	35	2023	4071
TBC_{hydr}	6	552	974

Conductivity of PEM based on double hydrophilic block copolymers which form IntraPCs

Table 2 - Conductivity of DBC and TBC membranes at a frequency 1 kHz

Copolymer	σ´, S·cm^{-1} at relative humidity :			
	33%	65%	81%	98%
DBC1	$1.12\cdot10^{-10}$	$3.32\cdot10^{-10}$	$8.79\cdot10^{-10}$	$1.97\cdot10^{-5}$
DBC2	$2.35\cdot10^{-10}$	$4.54\cdot10^{-10}$	$4.27\cdot10^{-9}$	-
DBC3	$2.57\cdot10^{-10}$	$2.31\cdot10^{-9}$	$1.13\cdot10^{-7}$	$6.61\cdot10^{-5}$
DBC_{hydr}	$7.89\cdot10^{-9}$	$4.67\cdot10^{-7}$	$9.95\cdot10^{-7}$	$9.68\cdot10^{-5}$
TBC1	$2.41\cdot10^{-11}$	$3.25\cdot10^{-10}$	$8.07\cdot10^{-10}$	$2.77\cdot10^{-6}$
TBC2	$1.50\cdot10^{-10}$	$3.15\cdot10^{-10}$	$1.64\cdot10^{-9}$	-
TBC3	$2.14\cdot10^{-10}$	$2.77\cdot10^{-10}$	$3.29\cdot10^{-9}$	$1.12\cdot10^{-6}$
TBC_{hydr}	$4.53\cdot10^{-10}$	$2.17\cdot10^{-7}$	$4.65\cdot10^{-5}$	$8.48\cdot10^{-4}$

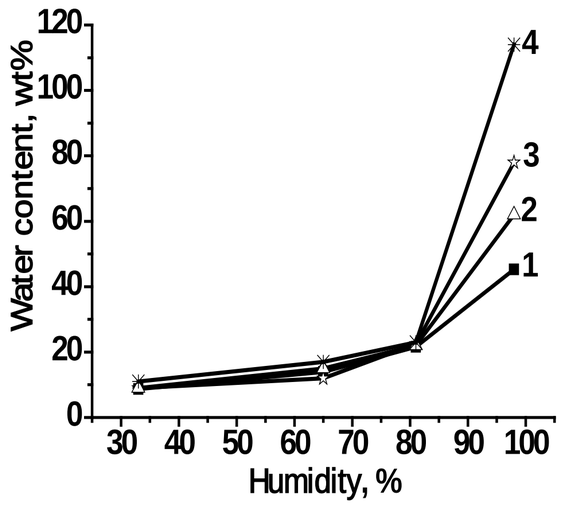


Fig. 1. Plot of water absorption vs. humidity SPE membranes comprising DBC1 – *1*; DBC2 – *2*; DBC3 – *3*and DBC_{hydr} – *4*

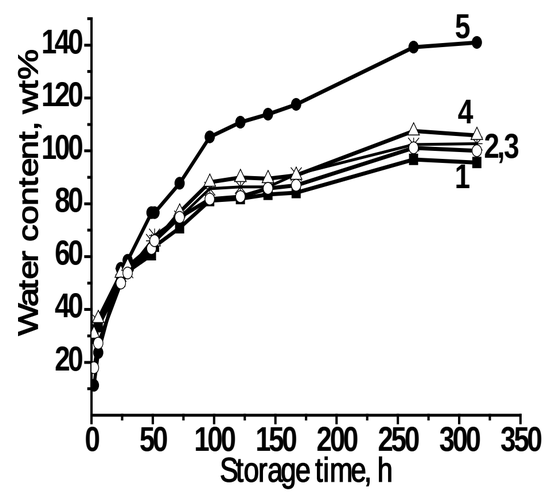


Fig. 3. Water absorption kinetics of SPE membranes comprising TBC1 –*1*; TBC2–*2*; DBC3 –*3*; TBC3 – *4* and TBC_{hydr} – *5*

Conclusion

In the present study, two series of SPE membranes, comprising diblock copolymers PEO-*b*-PAAm (DBC) and triblock copolymers PAAm-*b*-PEO-*b*-PAAm (TBC) of a variable PEO-block length were prepared and their electrochemical properties were investigated at ambient temperature and at different values of the relative humidity. The water absorption data show the rise of the absorbed water as the relative humidity grows in all the samples under study. It has been established that the conductivity of DBC and TBC membranes depends on the content of the adsorbed water and the PEO-block length. Introduction of -COOH-groups via partial hydrolysis of PAAm-blocks leads to the considerable increase in conductivity of the DBC and TBC membranes.